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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G21F 9/28	A2	(11) International Publication Number: WO 98/06106 (43) International Publication Date: 12 February 1998 (12.02.98)

(21) International Application Number: PCT/GB97/02057

(22) International Filing Date: 1 August 1997 (01.08.97)

(30) Priority Data:
9616264.9 2 August 1996 (02.08.96) GB

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: IONIC LIQUIDS AS SOLVENTS

(57) Abstract

A method of dissolving in an ionic liquid a metal in an initial oxidation state below its maximum oxidation state, characterised in that the ionic liquid reacts with the metal and oxidises it to a higher oxidation state. The initial metal may be in the form of a compound thereof and may be irradiated nuclear fuel comprising UO_2 and/or PuO_2 as well as fission products. The ionic liquid typically is nitrate-based, for example a pyridinium or substituted imidazolium nitrate, and contains a Bronstead or Franklin acid to increase the oxidising power of the nitrate. Suitable acids are HNO_3, H_2SO_4 and $[NO^+]$. Imidazolium nitrates and certain pyridinium nitrates form one aspect of the invention.

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IONIC LIQUIDS AS SOLVENTS

This invention relates to the reprocessing of irradiated fuel, as well as to a method for dissolving metal oxides in ionic liquids and to novel products or compositions of matter comprising ionic liquids.

By way of example, the irradiated fuel may be that resulting from the use of a fuel assembly in a light water reactor (LWR). Reference will be made below to such fuel but it should be understood that the invention is not restricted to the reprocessing of any particular type of irradiated fuel.

The irradiated fuel from an LWR is located within a Zircaloy cladding which has become oxidised as a result of the irradiation. In the known PUREX process for reprocessing irradiated fuel, the first stage involves the shearing and chopping of the fuel rods so that the irradiated fuel itself can be dissolved in nitric acid.

Molten salts are known for their use as solvents and they have in fact been proposed for use in the reprocessing of irradiated fuels from LWRs. These molten salts are typically mixtures of salts which are liquid only at high temperatures and offer little advantage as solvents over aqueous or organic media.

Recently, a salt, mixtures of salts, or mixtures of components which produce salts, which melt below or just above room temperature have become known. (In the terms of this invention, a salt consists entirely of cationic and anionic species). Such liquids are known as "ionic liquids" although this term can be used for salts which melt at relatively high temperatures, including for example temperatures of up to 100 °C. Common features of ionic liquids include a zero vapour pressure at room temperature, a high solvation capacity and a large liquid range (for instance, of the order of 300°C).

Known ionic liquids include aluminium(III) chloride in combination with an imidazolium halide, a pyridinium halide or a phosphonium halide. Examples include 1-ethyl-3-methylimidazolium chloride, *N*-butylpyridinium chloride and

tetrabutylphosphonium chloride. An example of a known ionic liquid system is a mixture of 1-ethyl-3-methylimidazolium chloride and aluminium(III) chloride.

E. S. Lane, J. Chem. Soc. (1953), 1172-1175 describes the preparation of certain alkylpyridinium nitrate ionic liquids, including sec-butylpyridinium nitrate. No use of the liquids is mentioned but reference is made to the pharmacological activity of decamethylenebis(pyridinium nitrate).

L. Heerman et al., J. Electroanal. Chem., 193,289 (1985) describe the dissolution of UO_3 in a system comprising *N*-butylpyridinium chloride and aluminium(III) chloride.

WO 96/32729 teaches that oxide nuclear fuels may be dissolved in a fused alkali metal carbonate to produce a compound which may be further processed so as to extract uranium therefrom.

WO 95/21871, WO 95/21872 and WO 95/21806 relate to ionic liquids and their use to catalyse hydrocarbon conversion reactions (e.g. polymerisation or oligomerisation of olefins) and alkylation reactions. The ionic liquids are preferably 1-(C_1-C_4 alkyl)-3-(C_6-C_{30} alkyl) imidazolium chlorides and especially 1-methyl-3-C_{10} alkyl-imidazolium chloride, or 1-hydrocarbyl pyridinium halides, where the hydrocarbyl group is for example ethyl, butyl or other alkyl.

The present invention provides in a first aspect the use of an ionic liquid containing an oxidant to dissolve a metal, optionally in the form of a compound thereof. The oxidant oxidises the metal to a higher oxidation state, which is normally more soluble in the ionic liquid than is the metal in its original oxidation state. More particularly there is provided a method of dissolving in an ionic liquid a metal in an initial oxidation state below its maximum oxidation state, characterised in that the ionic liquid reacts with the metal and oxidises it to a higher oxidation state.

As used herein, the term "metal" includes not only metallic elements in the (0) oxidation state but also metals in an oxidation state greater than zero, bonded to other

The products described in the preceding paragraph may often be viewed in a notional sense as comprising an ionic liquid base to which has been added an agent to increase the oxidising reactivity of the liquid. The nature of the notional "base" ionic liquid is not critical to the invention but preferred liquids comprise nitrate anion and an organic cation, especially nitrogen heterocycles containing a quaternary nitrogen, such as pyridinium or substituted imidazolium ions, for example. Exemplary ionic liquids include 1-butylpyridinium nitrate, 1-octylpyridinium nitrate, 1-butyl-3-methylimidazolium nitrate, 1-hexyl-3-methylimidazolium nitrate and 1-octyl-3-methylimidazolium nitrate.

The invention provides in addition novel nitrate-based ionic liquids, including those containing imidazolium and phosphonium cations as well as those containing pyridinium cations other than such cations disclosed by E. S. Lane.

Particularly preferred and novel ionic liquids are 1-butylpyridinium nitrate and 1-octylpyridinium nitrate. These products themselves, free from any oxidation enhancer, forms one aspect of the invention. To avoid ambiguity it should be stated that systematic names are used herein for individual compounds or moieties, i.e. "butyl" here refers to the group sometimes called n-butyl (CH_3-CH_2-CH_2-CH_2-).

The invention also includes ionic liquids which are compound mixtures of ionic liquids, for example ternary liquids, the constituent liquids of which can in combination achieve dissolution (typically by oxidising reaction) of inter alia selected substrates or substrate concentrations which the individual liquids cannot so achieve.

The invention includes further the use in a method for reprocessing an irradiated fuel of an ionic liquid to dissolve the fuel, as well as reprocessing methods which include the step of dissolving the fuel in an ionic liquid.

The present invention, therefore, relates to the use of ionic liquids as solvents, optionally after first serving as a reactive medium.

The Solvent

The solvent comprises an ionic liquid which usually contains an agent or species to make the solvent oxidisingly reactive to inter alia selected substrates, although this agent is not necessarily present in all aspects of the invention (as explained below under the heading "The Metal"). The agent may be an oxidant dissolved in a non-oxidising liquid or an auxiliary agent to increase the oxidising reactivity of another oxidising species. If the solvent contains nitrate ions, the agent increases the oxidising reactivity of the solvent beyond that which would be provided by the nitrate ions themselves; as described above such agents include Bronsted and Franklin acids.

The solvent may in principle comprise any ionic liquid but the liquid normally comprises nitrate anions.

The cation will in practice comprise one or more organic cations, especially nitrogen heterocycles containing quaternary nitrogen and more especially *N*-substituted pyridinium or *N,N'*-disubstituted imidazolium. The substituents are preferably hydrocarbyl and more preferably alkyl, which may be branched. for example. The hydrocarbyl (e.g. alkyl) groups usually contain from 1 to 18 carbon atoms and some usually from 1 to 8 carbon atoms.

The cation may therefore be a disubstituted imidazolium ion where the substituent groups take the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups. In preferred disubstituted imidazolium ions one substituent has n=1, 2 or 3 (of which methyl is particularly preferred) and the other has n=4, 5, 6, 7 or 8 (of which octyl, hexyl and more particularly C_4 especially butyl are preferred). Linear groups are preferred. Alternatively, the cation might be a substituted pyridinium ion, where the substituent group also takes the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups; suitable substituents include butyl, 2-(2-methyl)propyl, 2-butyl and octyl but straight chain alkyl, especially butyl, is preferred.

Of course, minor quantities of contaminants may be present, e.g. methyl imidazolium in 1-butyl-3-methyl imidazolium.

It will be appreciated from the above that the ionic liquids may be nitrate-based, i.e. have nitrate as anion. Ionic liquids comprising nitrate are new and included in the invention except for certain alkylpyridinium nitrates and polymethylenebis (pyridinium nitrate) compounds taught by Lane. Also novel is the use of nitrate-containing ionic liquids as a reactive medium or solvent. The ionic liquids of the invention comprise nitrate and a cation component which is not exclusively an alkylpyridinium nitrate or a polymethylenebis (pyridinium nitrate). However 1-butylpyridinium nitrate is a particularly preferred ionic liquid which is novel and is also included in the invention. Products comprising the new ionic liquids form an aspect of the invention.

The new nitrate-based ionic liquids may be prepared by mixing aqueous silver(I) nitrate together with an appropriate organic halide. By way of example, one such ionic liquid is prepared by mixing together solutions of aqueous silver(I) nitrate and 1-butyl-3-methylimidazolium chloride (bmim). Silver chloride is precipitated and the liquid 1-butyl-3-methylimidazolium nitrate is formed:

$$Ag[NO_3](aq) + [bmim]Cl(aq) \rightarrow AgCl(s) + [bmim][NO_3](aq)$$

The product may be purified by filtration and removing excess water from the filtrate.

1-hexyl-3-methylimidazolium nitrate is prepared by a similar method and this material is also a liquid at room temperature.

Alternative cations to pyridinium and imidazolium include quaternary phosphonium cations, e.g. tetra(hydrocarbyl) phosphonium. Suitable hydrocarbyl groups are as described above in relation to pyridinium and imidazolium cations.

The agent to increase the oxidising power of the ionic liquid (when used - see below under the heading "The Metal") is typically a Bronsted acid (e.g. HNO_3 or H_2SO_4) or a

Franklin acid, for example [NO^+], serving in either case to make nitrate more oxidisingly reactive towards substrates such as, for example, UO_2 and PuO_2. In other words, one class of ionic liquids of the invention contains an oxidant comprising nitrate and a promoter therefor. The oxidant when combined with the ionic liquid may react with the ionic liquid to create a new species which is also an ionic liquid. Thus, [NO][BF_4] is believed to react with the nitrate salts of organic cations to form the tetrafluoroborate(III) salt of the cation. An exemplary reaction is:

$$[\text{Bu-py}][NO_3] + [NO][BF_4] \rightarrow N_2O_4 + [\text{Bu-py}][BF_4]$$

wherein Bu-py is 1-butylpyridinium. [Bu-py][BF_4] is novel and included in the invention. The result of the reaction is a ternary ionic liquid. The invention includes the use of other compound ionic liquids.

The reaction of a tetrafluoroborate(III) salt and an ionic liquid results in an **anhydrous** tetrafluoroborate(III) product. The preparation of tetrafluoroborate(III) salts by such reactions is novel and included in the invention; such a preparative technique finds particular application in the making of organic tetrafluoroborate(III) salts, for example imidazolium, pyridinium and phosphonium salts.

Accordingly, the ionic liquid may comprise organic cations as described above and tetrafluoroborate(III) anions, e.g. be the tetrafluoroborate(III) salt of a quaternary nitrogen-containing heterocycle.

<u>The Metal</u>

The identity of the metal is not critical to the invention. In one aspect. the metal prior to dissolution is in a relatively low oxidation state and the ionic liquid composition is oxidising. Preferably, the metal prior to dissolution is in a state less soluble in the ionic liquid than when it is in a higher oxidation state and the ionic liquid composition is oxidising. The metal is typically in the form of an oxide. Preferred metal oxides include a variety of oxides of uranium. and plutonium(IV) oxide. Thus, by way of an

example only, UO_2 may be reacted with an ionic liquid which oxidises the uranium(IV) species to uranium(VI) species, e.g. oxidises uranium dioxide to *trans*-dioxouranium(VI) in complexed form. Similarly, plutonium(IV), normally as PuO_2, may be reacted with an ionic liquid which oxidises the plutonium(IV) to plutonium(VI), e.g. oxidises plutonium dioxide to *trans*-dioxoplutonium(VI) in complexed form.

In one class of embodiments, the metal oxides comprise plutonium and uranium oxides, primarily in the form of irradiated nuclear fuel, for example an irradiated fuel rod. Nuclear fuel rods consist of fuel pellets contained in cladding and the invention contemplates that the cladding is removed by the oxidising ionic liquid. The cladding is usually a zirconium alloy, for example that sold under the trade mark Zircaloy. In another embodiment of this invention, therefore, the ionic liquid may be used to dissolve an elemental metal (which expression includes alloys), which may be cladding material or may be irradiated metal fuel, e.g. uranium metal which contains fission products and actinides and which started its life either as pure uranium metal or an alloy of uranium and at least one other metal.

In some aspects, the invention relates to ionic liquids which do not contain an acid or other oxidation promoter. Thus, nitrate-based ionic liquids without an additional acid may be used as a reactive medium or a solvent. For example, they may be used as a reactive medium to oxidise substances capable of oxidation by nitrate. A suitable oxide for dissolution in such nitrate-based solvents might include and thorium(IV) oxide.

The Method

The invention is not restricted as to the manner in which the metal is dissolved in the ionic liquid solvent. Normally, the dissolution is performed at an elevated temperature of 50 °C or more, e.g. of up to 350 °C. Most preferably, the elevated temperature is from 50 °C to 100 °C. The metal is normally dissolved with the aid of agitation, typically stirring.

The resultant solution may be further processed, for example for the selective removal of particular species. In particular, uranium and plutonium may be separated from each other by such selective removal techniques; alternatively, a mixed uranium/plutonium oxide may be separated from other components of the solution. Known electrodeposition techniques may be used to extract uranium and/or plutonium species from the solution, whereby fission products remain in solution and the solution may then be subjected to pyrohydrolysis to provide oxides ready for disposal. Other chemical processes may be used to provide a stable wasteform for disposal. Alternatively, a method similar to the known PUREX process involving solvent extraction techniques may be used after the initial dissolution of the fuel in an ionic liquid. In this method, the fuel, and preferably the cladding, is dissolved in an ionic liquid and several extraction stages are carried out to remove fission products from the ionic liquid system and to separate the uranium product from the plutonium product ready for their subsequent reuse.

The invention preferably relates to the reprocessing of irradiated nuclear fuel. In one method, a fuel rod is placed in an oxidising ionic liquid and first cladding and then uranium and plutonium are dissolved in the ionic liquid. The uranium and optionally the plutonium are recycled into new fuel rods, e.g. by a method known per se, after being extracted from the ionic liquid. One class of methods includes the step of rupturing the cladding mechanically to expose the fuel pellets to the ionic liquid. In another method, the fuel rod is placed initially in a first ionic liquid for dissolving the cladding and subsequently in a second ionic liquid for dissolving the uranium and plutonium. The uranium and plutonium are normally as oxides thereof.

Those methods of the invention which concern the reprocessing of nuclear fuel may comprise performing one or more steps to process the dissolved fuel to form an intermediate or final nuclear fuel product, e.g. a gel, a powder, a pellet, a fuel rod or a fuel assembly.

The invention may be used in the reprocessing of any irradiated fuel, for example LWR, fast reactor and metal fuels. It may also be used to obtain purified dioxouranium(VI) nitrate from uranium ore or uranium ore concentrate ("yellow cake").

The invention is illustrated by the following Examples.

Examples

In the Examples, the following abbreviations are used:

Bu	:	butyl
Hex	:	hexyl
mim	:	methylimidazolium
Oct	:	octyl
py	:	pyridinium

^{1}H n.m.r abbreviations

s	:	singlet
d	:	doublet
t	:	triplet
quin	:	quintuplet
sex	:	sextuplet
m	:	multiplet
br	:	broad

Example 1

Chemicals

Solid UO_2 from BNFL, $UO_2(NO_3)_2{\cdot}6H_2O$ from BDH and nitronium tetrafluoroborate(III) ([NO][BF_4]) from Aldrich were all used as supplied.

1-Methylimidazole was distilled under vacuum and stored under dinitrogen prior to use. 1-Alkyl-3-methylimidazolium or 1-alkylpyridinium salts were prepared by direct reaction of the appropriate alkyl halide or haloalkane with 1-methylimidazole or pyridine, respectively, and recrystallised from ethanenitrile and ethyl ethanoate.

Spectra

UV-visible spectra were run in 1 mm pathlength cuvettes with quartz windows, referenced against a blank of the appropriate pure ionic liquid. Infrared spectra were recorded as thin films using NaCl plates.

Preparation of Nitrate Ionic Liquids

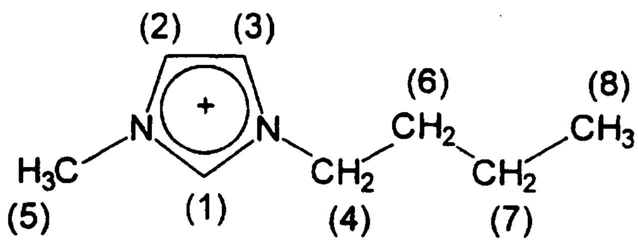
Nitrate ionic liquids were all prepared by methods analogous to the following method used to prepare 1-butyl-3-methylimidazolium nitrate.

1-butyl-3-methylimidazolium chloride (8.04 g, 46.0 mmol) was dissolved in water (15 cm^3). To this solution a solution of silver(I) nitrate (7.82 g, 46.0 mmol) in water (20 cm^3) was added. A white precipitate (possibly silver(I) chloride) formed immediately. The mixture was stirred (20 min) to ensure complete reaction, and was then filtered twice through a P3 sintered glass funnel to remove the white precipitate (the second filtration was generally necessary to remove the final traces of precipitate). The water was removed on a rotary evaporator, yielding a yellow or brown viscous liquid, sometimes containing small black solid particles. This crude product, 1-butyl-3-methylimidazolium nitrate, was dissolved in a small quantity of dry acetonitrile, and decolourising charcoal was added to the solution. This was then stirred (30 min) and filtered through Celite®. The acetonitrile was removed under vacuum, and the pale yellow ionic liquid product then dried by heating *in vacuo* (*ca.* 50 °C, 2-3 d). Some discoloration of the product occurred if the heating was too vigorous. The resulting ionic liquid was stored under dinitrogen to exclude moisture.

The [1]H n.m.r. spectra and microanalyses of the nitrate-based ionic liquids prepared following this procedure are shown below:

[Bu-mim][NO_3] ($CDCl_3$, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration	Proton identity (see figure)
9.86	s	1H	1
7.45	s	1H	2
7.38	s	1H	3
4.24	t	2H	4
4.02	s	3H	5
1.88	quin	2H	6
1.37	sex	2H	7
0.95	t	3H	8



Microanalysis: % found (calculated value): C = 45.60 (47.73); H = 7.58 (7.52); N = 20.04 (20.89).

[Hex-mim][NO_3] ($CDCl_3$, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration
9.65	s	1H
7.54	s	1H
7.46	s	1H
4.23	t	2H
4.00	s	3H
1.87	quin	2H
1.29	br	6H
0.86	t	3H

The spectrum shows that the sample was also contaminated with 1-methylimidazole.

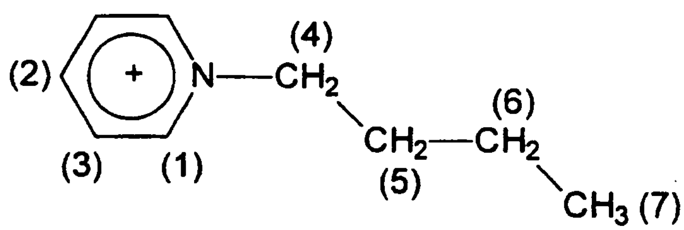
[Oct-mim][NO_3] ($CDCl_3$, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration
9.79	s	1H
7.56	s	1H
7.46	s	1H
4.26	t	2H
4.01	s	3H
1.89	quin	2H
1.31 + 1.25	br	10H
0.87	t	3H

The spectrum also shows small traces of 1-methylimidazole.

[Bu-py][NO_3] ($CDCl_3$, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration	Proton identity (see figure)
9.30	d	2H	1
8.51	t	1H	2
8.11	t	2H	3
4.80	t	2H	4
2.01	quin	2H	5
1.39	sex	2H	6
0.95	t	3H	7



Microanalysis: % found (calculated value): C = 50.56 (54.53); H = 7.35 (7.12); N = 13.50 (14.13).

[Oct-py][NO_3] ($CDCl_3$, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration
9.27	d	2H
8.50	t	1H
8.11	t	2H
4.78	t	2H
2.02	m	*
1.32 + 1.23	br	10H
0.85	t	3H

* integration slightly incorrect due to overlap with signal from traces of CH_3CN.

[Oct-py][NO_3] (neat liquid, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration
9.44	d	2H
8.65	t	1H
8.20	t	2H
4.82	br	2H
2.04	s	*
1.94	br	2H
1.20 + 1.12 + 0.99	br	10H
0.60	t	3H

*CH_3CN trace impurity, used as reference. Peaks generally broader than in $CDCl_3$ solution.

Example 2

Preparation of 1:10 [NO][BF_4]:[Bu-py][NO_3]

Nitronium tetrafluoroborate(III) (0.121 g, 1.03 mmol) was added to 1-butylpyridinium nitrate (2.258 g, 11.4 mmol) with stirring. A green colour was observed around the solid pieces of [NO][BF_4] on initial addition, although this colour disappeared when the mixture was stirred for two days. In addition, evolution of a brown gas was observed. Infrared spectral evidence demonstrated the removal of water from the ionic liquids by [NO][BF_4]

Example 3

Preparation of 1:2 [NO][BF_4]:[Bu-py][NO_3]

Nitronium tetrafluoroborate(III) (0.910 g, 7.8 mmol) was added to 1-butylpyridinium nitrate (3.000 g, 15.1 mmol) with stirring. Brown fumes were evolved immediately, and the solution rapidly turned dark blue/green. On stirring overnight all of the [NO][BF_4] dissolved to give a blue/green solution which was much less viscous than the starting material, 1-butylpyridinium nitrate.

^{1}**H n.m.r.** (neat liquid, 30°C)

Chemical shift, δ /ppm	Multiplicity	Integration
9.37	d	2H
8.90	t	1H
8.41	t	2H
4.99	t	2H
2.22	br	2H
1.52	sex	2H
1.04	t	3H

Note that ppm values may be slightly incorrect due to lack of reference peak.

Example 4

Dissolution of UO_2 in 1:1 Nitrate Ionic Liquid: Nitric Acid Mixture

A 1:1 molar mixture of 1-butylpyridinium nitrate and concentrated nitric acid was prepared, as much excess water as possible being removed on a rotary evaporator. UO_2 (*c.a.* 0.01 g) was added to 0.5 cm^3 of this solution, and the mixture was first stirred (2h) at room temperature with no sign of reaction. It was then heated (80 to 90 °C, 6 h), during which time the solution turned yellow, with most of the UO_2 dissolved. The uv-visible spectrum of the product solution showed a band with fine structure centred at λ = 438 nm which is indicative of the presence of a complexed form of the $[UO_2]^{2+}$ ion.

Example 5

Dissolution of UO_2 in 1:10 $[NO][BF_4]$:[Bu-py]$[NO_3]$

UO_2 (0.02 g, 0.074 mmol) was added to the 1:10 $[NO][BF_4]$:[Bu-py]$[NO_3]$ mixture (1.656 g). Stirring at room temperature resulted in no change in colour of the mixture (pale yellow), so the mixture was then heated (90 °C, 5 h). At this stage most of the UO_2 had dissolved, and the solution was a more intense yellow colour. More UO_2 (0.101 g, 0.37 mmol) was added to the reaction mixture at this point, and heating

continued (100 °C, 48 h). At the end of this time a small amount of UO_2 remained undissolved, but the solution was an intense yellow colour. The uv-visible spectrum displayed a band with fine structure centred at $\lambda = 436$ nm, indicative of the presence of a complexed $[UO_2]^{2+}$ ion. The solid residue from the reaction was collected, and weighed (0.018 g), indicating that a total of 0.103 g UO_2 (0.38 mmol) had reacted with the ionic liquid.

Example 6

Dissolution of UO_2 in 1:2 $[NO][BF_4]$:[Bu-py]$[NO_3]$

UO_2 (0.059 g, 0.22 mmol) was added to a 1:2 $[NO][BF_4]$:[Bu-py]$[NO_3]$ (2.45 g) under dinitrogen to exclude any water. The mixture was heated (*ca.* 65 °C, 16 h), at the end of which all the black UO_2 had dissolved, giving a yellow solution. More UO_2 (0.140 g, 0.52 mmol) was added to the mixture, and the heating continued (*ca.* 65 °C, 44 h). At the end of this time the solution was an intense yellow colour, but an as yet unmeasured amount of UO_2 remained undissolved. Once again the uv-visible and infrared spectra gave clear evidence for the presence of a complexed form of the $[UO_2]^{2+}$ ion.

CLAIMS

1. A method of dissolving in an ionic liquid a metal in an initial oxidation state below its maximum oxidation state, characterised in that the ionic liquid reacts with the metal and oxidises it to a higher oxidation state.

2. A method of Claim 1, wherein the metal is more soluble in the ionic liquid when in its higher oxidation state than when in its initial oxidation state.

3. A method of Claim 2, wherein the metal in its initial oxidation state is as an oxide.

4. A method of Claim 3, wherein the metal in its initial oxidation state is UO_2 or PuO_2, or a mixture thereof.

5. A method of any of Claims 1 to 4, wherein the ionic liquid contains nitrate ions and an acid.

6. A method of Claim 5, wherein the acid is HNO_3, H_2SO_4 or $[NO^+]$

7. A method of Claim 6, wherein the ionic liquid containing $[NO^+]$ is obtainable by dissolving $[NO][BF_4]$ in an ionic liquid having nitrate anions.

8. A method of any of Claims 1 to 7, wherein the cations of the ionic liquid are nitrogen heterocycles containing quaternary nitrogen.

9. A method of Claim 8, wherein the cations are *N*-substituted pyridinium or *N,N'*-disubstituted imidazolium.

10. A method of Claim 9, wherein the cations are (C_1-C_8 alkyl) pyridinium or 1-(C_4-C_8 alkyl)-3-methylimidazolium.

11. A method of any of Claims 1 to 10, which is performed at a temperature of from 80 °C to 100 °C.

12. A method for reprocessing an irradiated fuel which includes the step of dissolving the fuel in an ionic liquid capable of oxidising the fuel.

13. A method of Claim 12 in which the fuel is dissolved in the ionic liquid together with its cladding.

14. A method of Claim 12 in which a first ionic liquid is used to dissolve the fuel's cladding and a second ionic liquid is used to dissolve the fuel itself.

15. A method of any of Claims 12 to 14 in which dissolved uranium is extracted from the ionic liquid by a solvent extraction or electrochemical method.

16. A method of any of Claims 12 to 15 in which the ionic liquid is as defined in Claim 4 and/or in any of Claims 5 to 7, and/or in which the oxidant is as defined in any of Claims 8 to 10 and/or in which the dissolving step is performed at a temperature of from 80 °C to 100 °C.

17. A method of any of claims 12 to 16 which comprises processing the dissolved fuel to form a nuclear fuel product.

18 . A method of dissolving a metal oxide, comprising combining it with a product comprising an ionic liquid and which reacts with the metal oxide to oxidise the metal to an oxidation state in which it is soluble in the ionic liquid.

19. An ionic liquid containing nitrate and a Bronsted or Franklin acid.

20. An ionic liquid capable of oxidising UO_2 to convert the uranium to U(VI).

21. An ionic liquid of Claim 20 which comprises nitrate anions and nitronium cations in concentrations sufficient to enable the liquid to react with UO_2 and oxidise the uranium to U(IV), the ionic liquid also containing tetrafluoroborate(III) and an organic cation.

22. A method of making an anhydrous organic tetrafluoroborate(III) salt, comprising reacting a tetrafluoroborate(III) salt with an ionic liquid.

23. A method of Claim 22, wherein the tetrafluoroborate(III) salt reacted with the ionic liquid is [NO][BF_4].

24. A method of Claim 22 or Claim 23, wherein the ionic liquid is the nitrate of a substituted imidazolium, pyridinium or phosphonium cation.

25. A product comprising 1-butylpyridinium nitrate or 1-octylpyridinium nitrate.

26. A nitrate-based ionic liquid provided that its cation component is not exclusively an alkylpyridinium nitrate or a polymethylenebis (pyridinium nitrate).

27. An imidazolium nitrate.

28. 1-butyl-3-methylimidazolium nitrate, 1-hexyl-3-methylimidazolium nitrate or 1-octyl-3-methylimidazolium nitrate.

29. A product comprising a nitrate of Claim 26, Claim 27 or Claim 28.

30. A product comprising 1-butylpyridinium tetrafluoroborate(III).

31. The use of a product of Claim 25 or Claim 29 or of a nitrate of any of Claims 26 to 28 in combination with an acid to dissolve uranium and/or plutonium in irradiated fuel.

32. A method of dissolving in an ionic liquid a metal in an initial oxidation state below its maximum oxidation state, characterised in that the metal is oxidised by the ionic liquid into an oxidation state in which it is more soluble in the ionic liquid than when it is in the initial oxidation state.

33. The use of an ionic liquid of which nitrate is a component as a reactive medium or solvent.

34. The use of Claim 33 wherein the ionic liquid contains an acid.

35. A method of making a nitrate-based ionic liquid of claim 25 or claim 26, comprising contacting together aqueous silver(I) nitrate and an appropriate organic halide.

36. A method of Claim 35 wherein the organic halide is an imidazolium halide.

37. A method of Claim 36 wherein the imidazolium halide is a 1-(C_4-C_8 alkyl)-3-methylimidazolium halide.

38. A method of Claim 37 wherein the imidazolium halide is a 1-butyl-3-methylimidazolium halide, a 1-hexyl-3-methylimidazolium halide or a 1-octyl-3-methylimidazolium halide.

39. The use in a method for reprocessing an irradiated fuel of an ionic liquid to dissolve the fuel.

40. The use of Claim 39 wherein the ionic liquid is nitrate-based and optionally imidazolium-based and/or wherein a first ionic liquid is used to dissolve the fuel's cladding and a second ionic liquid is used to dissolve the fuel itself.

elements, for example U(IV) and U(VI). Thus, the metal in its original oxidation state may comprise a metal compound, for example a metal oxide.

The metal preferably comprises uranium (typically as UO_2 and/or U_3O_8) or plutonium (typically as PuO_2), or both, and usually fission products. The UO_2 or PuO_2 is not directly dissolved in the oxidising ionic liquid but, rather, the oxide reacts with the ionic liquid to form an oxidised species which dissolves in the ionic liquid. Such preferred dissolution processes may be used in the reprocessing of an irradiated nuclear fuel. The invention also includes the use of the oxidising ionic liquid to dissolve other metal species, for example a zirconium alloy, which may be in the form of cladding of a nuclear fuel rod.

In another aspect, therefore, the invention provides a method of dissolving a metal in less than its maximum oxidation state in an ionic liquid, wherein one component of the ionic liquid is an oxidant to oxidise the metal to a higher oxidation state. The metal is typically in the form of an oxide thereof.

The invention further provides an ionic liquid comprising an agent to increase the oxidising power of the liquid, for example to make a non-oxidising liquid to be oxidising. Thus, the liquid will contain not just one anion and one cation but in addition another component which enhances the ability of the liquid to react to oxidise a substrate. In preferred embodiments, the liquid contains both the mildly oxidising anion $[NO_3^-]$ and an acid, which may be a Bronsted or Franklin acid such as HNO_3, H_2SO_4 or $[NO^+]$, e.g. from $[NO][BF_4]$. The acid makes the liquid more oxidisingly reactive towards various substrates, such as UO_2 and PuO_2, for example. Thus, the invention includes an ionic liquid capable of oxidising UO_2 to convert the uranium to U(VI), especially an ionic liquid which comprises nitrate anions and nitronium cations in concentrations sufficient to enable the liquid to react with UO_2 and oxidise the uranium to U(VI), the ionic liquid also containing tetrafluoro-borate(III) and an organic *cation*. A preferred product is an ionic liquid containing $[NO^+]$, typically having been added to the liquid as $[NO][BF_4]$.